EXPLORING OF THE TRANSESTERIFICATION OF CASTOR OIL TO PRODUCE BIODIESEL USING QUICKLIME AS A BASIC CATALYST

by

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LIST OF ABBREVIATIONS

CaO	Calcium oxide
FFA	Free fatty acids
EPA	Environmental Protection Agency
SFA	Saturated fatty acids
UFA	Unsaturated fatty acids
THF	Tetrahydrofuran
FAME	Fatty acid methyl ester
GC-MS	Gas Chromatography Mass Spectrometry
HC	Hydrocarbon
CO	Carbon monoxide
PM	Particulate matter
NO_X	Nitrogen oxides

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ABSTRAK

Pada dasarnya, kajian ini adalah untuk meneroka proses transesterifikasi terhadap minyak jarak untuk menghasilkan biodiesel dengan menggunakan kalsium oksida sebagai pemangkin. Objektif utama kajian adalah untuk menggunakan kalsium oksida sebagai pemangkin yang mungkin dapat menghasilkan kandungan biodiesel yang tinggi daripada minyak jarak. Dalam kajian ini, minyak jarak telah dipilih sebagai bahan mentah kerana ia telah dihasilkan di Malaysia dan merupakan minyak yang tidak boleh dimakan. Metanol telah dipilih sebagai pelarut kerana harganya yang lebih murah berbanding dengan alkohol yang lain. Melalui proses transesterifikasi, biodiesel dihasilkan apabila berlakunya tindak balas antara *triglycerides* (minyak jarak) dengan alkohol (metanol) dengan kehadiran pemangkin (kalsium oksida) untuk menghasilkan asid lemak metil ester (biodiesel) dan *glycerol*. Eksperimen ini dijalankan dengan menggunakan dua pembolehubah yang berbeza iaitu nisbah metanol kepada minyak (3:1 dan 4:1) dan masa (60 minit, 120 minit, dan 180 minit). Kepekatan pemangkin telah ditetapkan pada 1% dan suhu juga telah ditetapkan pada 60^{o}C. Sampel daripada setiap eksperimen telah dianalisis dengan menggunakan Gas Kromatografi Jisim Spektrometri. Berdasarkan keputusan eksperimen yang telah diperolehi, nilai kandungan biodiesel yang tertinggi adalah 82% pada keadaan 3:1 nisbah metanol kepada minyak, 180 minit, 1% kepekatan kalsium oksida dan suhu 60^{o}C.

ABSTRACT

This research is basically an experiment to exploring the transesterification of Castor oil to biodiesel using quicklime (CaO) as solid base catalyst. The objectives of this research are to use heterogeneous catalyst quicklime for possible high yield production biodiesel from castor oil. In this research, castor oil has been chosen as feedstock because it is readily available in Malaysia and non-edible oil. Methanol was chosen as alcohol solvent because its price is cheaper compare to other type of alcohol. Through a process called transesterification, biodiesel is made by reacting triglycerides (castor oil) with alcohol (methanol) in the presence of a catalyst (quicklime) to produce fatty acid methyl esters (biodiesel) and glycerol (co-product). This experiment was conducted with two different parameters which are methanol: oil ratio (3:1 and 4:1) and reaction time (60 minutes, 120 minutes and 180 minutes). The catalyst concentration was fixed at 1 wt% and the temperature was fixed at 60^{o}C. The sample of each experiment was analysed using Gas Chromatography Mass Spectrometry (GC-MS). The best yield biodiesel product was 82% at reaction conditions; 3:1 methanol/oil ratio, 180 minutes, 1 wt% of CaO and 60^{o}C.

CHAPTER 1

INTRODUCTION

1.1 General Background

With the rise in concern for pollution caused by fossil fuels such as petroleum, coal and natural gas, and the realization that energy supplies are not infinite, alternative fuels and renewable source of energy such as biodiesel are being considered worldwide.

In the United States and Europe, the requirement for transportation fuel has increased and this trend will continue. In developing countries, such as India, Malaysia, South Africa, Vietnam and China, energy use will continue to increase for economic growth and improved standards of living. With the increasing reliance on imported petroleum, these countries are extremely vulnerable to fuel price fluctuations and supply disruption.

Fossil fuels use in transportation is the leading contributor to urban air pollution and to global warming. The fossil fuels produced from petroleum, like gasoline and diesel, come in the category of non-renewable fuel and will last for limited period of time. In recent years, new sulfur and aromatic compound limits give the petroleum producers a new challenge to lower the sulfur and aromatic content of traditional fuel. The World Energy Forum predicted that fossil oil will be exhausted in less than 10 decades, if new oil wells not found (Sharma and Singh, 2009). Figure 1 presents the projection of energy demand for the new future, indicating that there is an urgent need to find more renewable energies sources to assure energy security world.

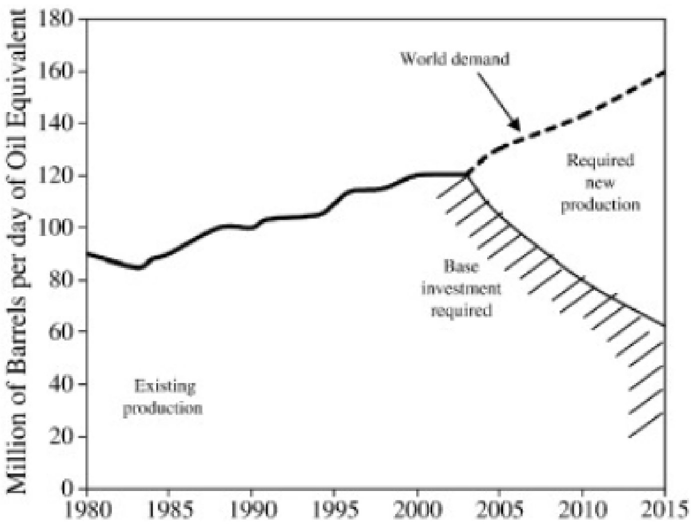

Figure 1.1: Projection of energy demands for the new future (Sources: Biotechnology Advances, 2010)

As a result, the cost associated with fuel-production and engine-modification will increase in order to meet the more stringent environmental legislation. People throughout the world are looking for effective, cost-competitive technologies to comply with current and pending regulations. Hence, vegetable oils are emerging as a great alternative fuel because of their renewable and environmental benefits (Sharma et al., 2009).

Biodiesel has been defined as a methyl-ester produced from vegetable or animal oil, of diesel quality, to be used as biofuel (Encinar, F. Gonzalez, Martinez, Sanchez and G. Gonzalez, 2010). Biodiesel obtained from different vegetable oils is being considered as a potential source of energy. This is mainly due to biodiesel being nontoxic and biodegradable which makes it an environmentally friendly fuel. In addition, the emissions of carbon dioxide, sulfur dioxide, unburned hydrocarbons, and particulate matter are reduced during the biodiesel combustion process. Generally speaking, biodiesel is obtained by the transesterification of triglycerides. These triglycerides are converted to the corresponding alkyl ester and glycerol by transesterification with short chain alcohols, typically methanol. The main purpose of transesterifying the vegetable oil is to lower its viscosity and raising the volatility. At the same time, improving its fuel quality applications in the compression-ignition (diesel) engine (Chakrabarti and Ahmad, 2008; Boey, Maniam and Abd. Hamid, 2011).

As a tropical country, Malaysia has a suitable climate and soil for cultivating the Castor trees. Castor oil is a very pale yellow liquid with mild or no odor. It is cultivated around the world because of the commercial importance of its oil is used in the manufacture of a number of industrial chemicals like surfactants, cosmetics and personal care products, pharmaceutical and other. The comparative advantage of castor is that its growing period is much shorter than that of Jatropha and Pongamia which can reach a height around 12 meters (Casa Kinabalu, 2012). In addition, there is considerably greater experience and awareness among farmers about its cultivation. Being an annual crop it gives the farmers the ability to rotate or shift away easily depending on market conditions.

1.2 Problem Statement

In the past few decades, fossil fuels mainly petroleum, natural gas and coal have been playing an important role as the major energy resources worldwide. However, these energy resources are non-renewable and are projected to be exhausted in the near future. This has caused the price of crude petroleum to hit a record high of USD (US dollar) 90 per barrel in October 2007 and still rising. Therefore, there is an urgent need to find a new energy resource that is renewable, clean, reliable and yet economically feasible as a substitution to the current fossil fuels. In this context, recently biodiesel derived from vegetable oil has been shown to be a potential alternative replacing petroleum-derived diesel oil for diesel engine. Although there is continuous increase in the production of vegetable oil, however the ending stocks of vegetable oils are continuously decreasing due to increasing production of biodiesel. Eventually, with the implementation of biodiesel as a substitute fuel for petroleum-derived diesel oil, this may lead to the depletion of edible-oil supply worldwide. So, castor oil is chosen as non-edible oil to produce biodiesel. The beans contains toxin that makes the oil and cake inedible. It was chosen for the study because it widely available, has no other commercial uses and unlike vegetable oils such as soya beans, would not compete for other uses such as consumption.

1.3 Research Objective

The objectives of this research are:

1. To use heterogeneous catalyst quicklime for possible high yield production biodiesel from castor oil.

2. To determine the effect of time reaction and methanol/oil ratio in transesterification process using calcium oxide as a basic catalyst.

1.4 Research Scope

This research is an experimental study in production of biodiesel using castor oil as the feedstock. In order to realize these research objectives, I used the time reaction of 1 hour, 2 hours and 3 hours. Besides that, I used the ratio of alcohol to oil of 3:1 and 4:1. While the catalyst concentrations and the temperatures are fixed at 1wt% and 60^{o}C.

1.5 Significance of Research

The significance of my research is to use non-edible vegetable oil as source of production biodiesel to maintain important of food oil. The use of non-edible vegetable oils as compared to edible oils is very significant in developing countries because of the tremendous demand for edible oils as food and they are far too expensive to be used as fuel at present.

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CHAPTER 2

LITERATURE REVIEW

2.1 The Current Status of Biodiesel

According to Kawashima, Matsubara and Honda (2009), biodiesel consist of methyl or ethyl esters derived from vegetable oil, animal fat, waste oil and microalgae oil through the process of transesterification.

In the early literature, there are several terminologies for these ester-forming reactions, namely alcoholysis, acidolysis and ester interchange but recently it is more common to use the term transesterification to describe the ester reaction, which when carried out with an alcohol in the presence of an acid or base catalyst is known as alcoholysis. Depending on the specific alcohol used, alcoholysis is referred to as methanolysis, ethanolysis, propanolysis, and butanolysis and other. In this project, methanolysis will be adhered to throughout this whole work.

Since the worldwide energy shortage and oil crisis in the late 1970's and early 1980's. Vegetable oils and waste oil have attracted attention as a potential renewable resource for the production of an alternative to petroleum-based diesel fuel. Various products from vegetable oils and waste cooking oils have been proposed as an alternative fuel for diesel engines. Researches also studied the biodiesel made from free fatty acids. This reaction is catalyzed by acid at elevated pressure.

Since biodiesel is made entirely from vegetable oil or animal fats, it is renewable and biodegradable. Biodiesel also contains very little sulphur, polycyclic aromatic hydrocarbons and metals (Vasudevan and Briggs, 2008). Petroleum-derived diesel fuels can contain up to 20% polycyclic aromatic hydrocarbons. For an equivalent number of carbon atoms, polycyclic aromatic hydrocarbons are up to three orders of magnitude more soluble in water than straight chain aliphatics. The fact that biodiesel does not contain polycyclic aromatic hydrocarbons makes it a safe alternative for storage and transportation. Biodiesel fuels can be used in regular diesel vehicles without making any changes to the engines, although older vehicles may require replacement of fuel lines and other rubber components (Vasudevan et al., 2008). Since biodiesel is oxygenated, it is a better lubricant than diesel fuel, increasing the life of engine and is combusted more completely. Indeed, many countries are introducing biodiesel blends to enhance the lubricity of low-sulphur diesel fuels. Researchers also found that the higher flash point of biodiesel makes it a safer fuel to use, handle and store. With its relatively low emission profile, it is an ideal fuel for use in sensitive environments such as heavily polluted cities.

There are some advantages of biodiesel as a substitute for diesel fuel. First and foremost, the transportation sector with its great demand for gasoline and diesel fuel relies almost exclusively on petroleum for energy. Biodiesel can be produced domestically from agricultural oils and from waste fats and oils. Because it can be used directly in diesel engines, biodiesel offers the immediate potential to reduce our demand for petroleum. The burning of fossil fuels during the past century has dramatically increased the levels of carbon dioxide and other greenhouse gases that trap heat in our atmosphere. Their implications are hotly debated, but the levels of these gases have unquestionably risen at unprecedented rates in the context of geological time. To the extent that biodiesel is truly renewable, it could help reduce greenhouse gas emissions from the transportation sector. Since regular diesel engines like those in tractor trailer trucks and heavy construction equipment can use biodiesel in their existing engines, it is one of the simplest alternative fuels to use.

2.2 Comparison of Diesel and Biodiesel

The most commonly used fuel that contains biodiesel is a mixture of 20% biodiesel and 80% regular petroleum diesel called B20. Fuel that is 100% biodiesel is called B100. Table 2.1 presents properties comparison for diesel, B20 and B100.

Table 2.1: Properties of diesel and biodiesel (Tyson, Bozell, Wallace, Eugene and Moens, 2004)

Fuel Type	Density (g/cm^3)	Average Net Heating Value (Btu/gal)	% Difference from No. 2 Petro Diesel
No. 2 Petro Diesel	0.85	129 500	
Pure Biodiesel (B100)	0.88	118 296	8.65 %
Blend Diesel (B20)	0.856	127 259	1.73 %
Blend Diesel (B2)	0.851	129 276	0.17 %

Energy content of petro diesel can vary up to 15%. The energy content of biodiesel is much less variable than that of petro diesel. The feedstock utilized has a greater effect on the energy content of biodiesel than a particular processing method.

Pure biodiesel contains about 8% less energy per gallon than No. 2 petro diesel or 12.5% less energy per pound. This difference results from the slightly higher density of biodiesel than petro diesel, 0.88 kg/L versus 0.85 kg/L. As the ratio of biodiesel to petro diesel becomes lower, any difference between the biodiesel and petro diesel becomes less significant. B20 and B2 have 1.7% and 0.17% less energy per gallon from the petro diesel respectively and do not exhibit a noticeable difference in performance (Tyson et al., 2004).

Pure biodiesel contains up to 10-12% weight of oxygen, while diesel contains almost 0% oxygen. The presence of oxygen allows more complete combustion, which reduces hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM) emission. However, higher oxygen content increases nitrogen oxides (NOx) emissions.

The primary reason biodiesel is suitable as an alternative fuel for petro diesel lies in the cetane number. The cetane number indicates the ignition quality of a diesel fuel. It measures a fuel's ignition delay, which is a period between the start of injection and start of combustion (ignition) of the fuel. Fuels with a higher cetane number have shorter ignition delays, providing more time for the fuel combustion process to be completed. The term "cetane number" is derived form a straight chain alkane with 16 carbons ($C_{16}H_{34}$), hexadecane or cetane which is shown in Figure (2.1).

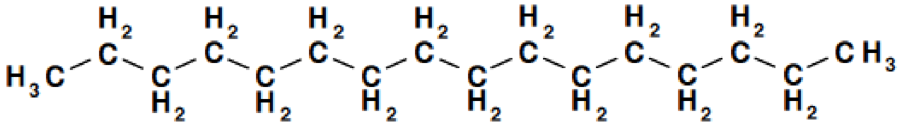

Figure 2.1: Hexadecane

This long unbranched hexadecane is the high quality standard on the cetane scale and has been assigned as having a cetane number of 100. On the other hand, highly branched alkanes are low quality compounds on the cetane scale and have low cetane numbers. Biodiesel's long chain fatty acids methyl ester are similar to long chain alkanes with number of carbons ranging from 14 to 22 (Figure 2.2). This makes biodiesel suitable for alternative diesel fuel (Gerpen, Shanks and Pruszko, 2004).

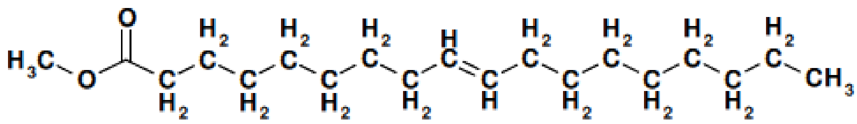

Figure 2.2: Fatty acid methyl ester

From table below, many other hazardous by-products of the combustion of diesel fuel are reduced.

Table 2.2: Average biodiesel emissions compared to conventional diesel according to EPA

Emission Type	B100	B20
Total Unburned Hydrocarbons	-67%	-20%
Carbon Monoxide	-48%	-12%
Particulate Matter	-47%	-12%
NO_x	+10%	+2% - -2%
Sulphates	-100%	-20% (estimated from B100)

This EPA (Environmental Protection Agency) study shows biodiesel is a much safer alternative to diesel fuel as proven by the reduced emissions in the majority of categories. The only category in which biodiesel had higher emissions was Nitrogen Oxides or No_x. However, the lack of sulphates present in biodiesel allow for nitrogen oxide reduction technologies or fuel additives to be used that could not be used otherwise if burning diesel fuel. This substantial reduction in the amount of emissions produced makes biodiesel an extremely attractive alternative to traditional biodiesel fuel.

2.3 Non-edible Oil

The example of non-edible oil use for biodiesel production includes Jatropha, Rubber seed, Castor and Pongamia plunata. The most commonly use was Jatropha Curcas which widely use in India and Indonesia because of its easy availability growth in arid, semiarid and wasteland (Ghadafi, 2008). Castor oil has long been used as lubricant in engines but only recently has research on the use of Castor oil has a biofuel started (Nielsen, Hill and Jongh, 2011). The oil yield for major non-edible and edible oil sources are shown in Table 2.3.

Table 2.3: Oil yield for major non-edible and edible oil sources (Shirame et al., 2011)

Type of oil	Oil yield (kg oil/ha)	Oil yield (wt %)
Non-edible oil		
Jatropha	1590	Seed: 35-40 Kernel: 50-60
Rubber seed	80-120	40-50
Castor	1180	53
Pongamia plunata	225-2250	30-40

Edible oil		
Soybean	375	20
Palm	5000	20
Rapeseed	1000	37-50

From the table, it showed that the oil yield for non-edible oil is higher compared with edible oil.

2.4 Castor oil

Castor oil is obtained from pressing castor beans (the seeds of a plant which has the botanical name Ricinus communis of the family Eurphorbiacae. This is done by either one or a combination of mechanical pressing or solvent extraction. The oil is a pale yellow, viscous, non-volatile and non-drying with a bland taste. It finds uses as a purgative, a plastic and textile finishing material, in paints and varnishes, a feedstock to the transesterification process for the production of biodiesel as well as in the beauty industry as a cosmetic and hair oil. Castor oil has an advantage over other mineral oil in that it is biodegradable, eco-friendly and renewable resource (Ogunniyi, 2006).

Castor oil is a triglyceride in which 80-90% of fatty acid chains are ricinoleic acid. No other vegetable oil contains so high a proportion of fatty hydroxy acids (Shrirame, Panwar and Bamniya, 2011). Oleic, linoleic acids and saturated fatty acids are the other significant components which 2-4% oleic acid, 3-6% linoleic acid and 1-5% saturated fatty acids (Pena, Romero, Luz Martinez, Ramos, Aldo Martinez and Natividad, 2009). Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstocks. In Malaysia, there also castor plant which is at Kuching, Sarawak but the uses of castor oil is not widely applied. Its fruits are produced in typical clusters, each pod containing well developed seeds bearing sufficient oil (47-49%).Castor oil has excellent solubility in methanol and hence theoretically ideal oil for transesterification to biodiesel, requiring a minimum amount of catalyst and heating which can reduce costs production (Bello and Makanju, 2011).

Castor grows well under hot and humid tropical conditions and has a growing period of 4 to 5 months. Castor oils unsaturated bond, high molecular weight (298), low melting point (5^oC) and very low solidification point (-12^oC to -18^oC) make it industrially useful, most of all for the highest and most stable viscosity of any vegetable oil (Shrirame et al., 2011). The characteristics of Malaysian castor seed oil are shown in Table 2.4. The fatty acids composition of castor oil is shown in Table 2.5.

Table 2.4: Characteristics of Malaysian Castor seed oil (Salimon, Noor, Nazrizawati, Firdaus and Noraishah, 2010)

Parameters	**Value**
Lipid content (%)	43.3
Moisture content (%)	0.2
Iodine value (mg/g)	84.5
Acid value (mg/g)	4.9
% free fatty acid	3.4
Peroxide value (meq/kg)	10.2
Saponification value (mg/g)	182.9
Unsaponificable value (mg/g)	3.4
Viscosity	332
Refractive Index at 25^oC	1.47
Average molecular weight	937.7

Table 2.5: Fatty acids composition of Malaysian Castor seed oil (Salimon et al., 2010)

Fatty acid	Percentage		
	Malaysia	**Brazil**	**India**
Palmitic	1.3	0.7	-
Stearic	1.2	0.9	1.0
Oleic	5.5	2.8	-
Linoleic	7.3	4.4	4.3
Linolenic	0.5	0.2	-
Ricinoleic	84.2	90.2	94.0
Saturated fatty acids (SFA)	2.5	1.6	1.0
Unsaturated fatty acids (UFA)	97.5	97.6	98.3

From an energy point view, Castor oil is the best vegetable oil for producing biodiesel (Castor methyl ester or Castor ME) because it does not require heat and the consequent energy that is needed when other vegetable oils are transformed into biodiesel. Long storage times are unproblematic under airtight conditions. Biodiesel made from Castor oil still has a relatively high viscosity. In Brazil, Castor ME was found too viscous to be used as such and is blended with biodiesel from other vegetable oils (Nielsen, Hill and Jongh, 2011). Furthermore, Castor oil tends to have same characteristics as other vegetable oils; however it’s only produce a little glycerol. Castor oil has only 5.1-6.1% of glycerol. Meanwhile the ester produced from the castor oil is more than the other vegetable oils, which is between 84-92% (Zuhdi, Gerianto, Hashimoto and Dan, 1998).

2.5 Production of Biodiesel

Ma and Hanna (1999) have examined experimentally four primary ways to produce biodiesel. There are direct use and blending, microemulsions, thermal